

The Effect of Hydrogen Bonding on the Phase Behavior of Poly(ethylene-co-acrylic acid)-Ethylene-Cosolvent Mixtures at High Pressures

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Abstract—Experimental cloud-point data to 260 °C and 2,500 bar are reported to demonstrate the impact of two cosolvents, acetone and methanol, on the phase behavior of polyethylene, poly(ethylene-co-2.4 mol% acrylic acid) (EAA_{2.4}), poly(ethylene-co-3.9 mol% acrylic acid) (EAA_{3.9}), poly(ethylene-co-6.9 mol% acrylic acid) (EAA_{6.9}), and poly(ethylene-co-9.2 mol% acrylic acid) (EAA_{9.2}) in ethylene. In pressure-temperature (P-T) space, the miscibility of EAA copolymers in ethylene decreases significantly with temperature and with increasing acrylic acid content of EAA due to self-association of the acrylic acid segments. Acetone and methanol, both dramatically enlarge the solubility of EAA copolymers due to the hydrogen bonding with acrylic acids in the EAA. At low concentrations, methanol is a better cosolvent than acetone. However, the impact of methanol diminishes rapidly with increasing methanol concentration once all the acrylic acids in the EAA are hydrogen bond with methanol molecules.

Key words: Poly(ethylene-co-acrylic acid), Hydrogen Bond, Cosolvent, Phase Behavior, High Pressures

INTRODUCTION

Since first being developed in the early 1940s, low density polyethylene (LDPE) has been one of the most widely used thermoplastics in the world. Although LDPE is polymerized under kilo-bar pressure conditions, it has many desirable properties such as clarity, sealability, and chemical inertness as well as a low price. However, Ziegler-Natta catalyst made it possible to polymerize ethylene at relatively low pressures to high density polyethylene (HDPE) and linear low density polyethylene (LLDPE). Now LDPE and HDPE are competing in the PE markets and LDPE plants have been converted to produce specialty copolymers. Within the past 25 years, much attention has been given to ethylene-based copolymers that can be commercially produced by free radical polymerization under high pressures, similar to the conventional LDPE. Ethylene-based copolymers have properties sufficiently different relative to the homopolymer LDPE. For instance, poly(ethylene-co-methyl acrylate) (EMA) has superior thermal stability, stress crack resistance, and adhesive strength relative to LDPE [Baker, 1991; Kaus, 1988]. Poly(ethylene-co-acrylic acid) (EAA) and poly(ethylene-co-methacrylic acid) (EMAA) also have excellent strength, toughness, adhesive strength, and chemical resistance than PE does [Mergenhausen, 1991; Brentin, 1988]. Due to the superior properties, ethylene-based copolymers are sold at 3 to 10 times higher prices than LDPE. The different properties of the ethylene-based copolymers are a consequence of the incorporation of a comonomer into polyethylene. During the copolymerization, a small change of comonomer concentration in the feed can cause a great change of comonomer composition in the copolymer. The physical properties of the copolymer vary not

only with molecular weight and degree of chain branching but also with composition of comonomer in the copolymer, the copolymerization may take place in heterogeneous phase. Because of the wide variation in copolymer properties, the phase behavior of copolymer-solutions can be rather unpredictable. Therefore, it is important to know the location of the phase boundaries for copolymer solutions in order to avoid potential fouling problems or runaway reactions which may occur if a two-phase region is allowed to form inside the reactor. An understanding of the high-pressure phase behavior of copolymer solutions is also needed to efficiently separate product copolymers from unreacted monomers recycled to the reactor. However, the determination of phase boundaries in ethylene-based copolymers is not a trivial problem, since ethylene copolymers are typically produced at pressures in the range 2,000-3,000 bar, and at temperatures as high as 250 °C [Boysen, 1981].

A large number of studies have been conducted to determine the phase behavior of ethylene-based copolymers [LoStracco et al., 1994; Gregg et al., 1994a, b; Hasch et al., 1993b; Luft and Wind, 1992]. Hasch et al. [1992, 1993a] Meilchen, et al. [1992] and Pratt et al. [1993] determined the cloud-point behavior of poly(ethylene-co-methyl acrylate) (EMA) in ethane, ethylene, propane, propylene, butane, and butene. They determined the cloud-point curves with four different EMA that the methyl acrylate contents in the EMA are 10, 18, 31, and 41 mol%. They demonstrated that the one-phase regions of EMA - alkane solutions are reduced as the methyl acrylate contents in the backbone structures of EMA increase. This phase behavior is a consequence of strong polar interactions between methyl acrylate repeat units. However, the one phase region of EMA - alkene mixtures enlarges at low methyl acrylate contents in EMA, then shrinks as the methyl acrylate contents increase. Lee et al. [1994a, b] reported the high-pressure solution behavior of EAA in low molecular weight hydrocarbon solvents and dimethyl ether (DME). They

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concluded that the phase behavior of EAA - hydrocarbon solvent mixtures can be dominated by even a small number of acrylic acid units in the backbone of copolymer due to the strong dimerization energy between acrylic acid segments. They also showed that the acid content in the copolymer has a much greater effect on the phase behavior than does molecular weight. Interestingly, they found that the cloud-point curves for the EAA - butene system order with respect to M_n rather than M_w . They interpreted that the ordering of the EAA - butene cloud-point curves with M_n is a result of intrapolymer hydrogen bonding that depends on the number of acid groups rather than on their weight.

Several studies were performed to investigate cosolvent effect on the ethylene-based acid copolymers [Lee and McHugh 1997; Lee et al., 1996]. Luft and Wind [1992] reported that the phase behavior of EAA ethylene mixtures was influenced by the dimerization of the acrylic acid groups in EAA even at 220 °C. Lee et al. [1997] showed that adding a polar cosolvent, DME and ethanol, to non-polar butane has a dramatic impact on the conditions needed to dissolve EAA copolymers. DME and ethanol both hydrogen bond with the acrylic acid units of EAA, which reduces the pressures and temperatures needed to dissolve this copolymer relative to the conditions needed when pure butane is used. They reported that the impact of both DME and ethanol diminishes at cosolvent concentrations greater than ~15 wt% since unfavorable polar interactions between excess cosolvent molecules increase once all the acid sites in EAA are saturated with cosolvent. They also showed that as temperatures decrease ethanol reverts to antisolvent behavior at high concentrations since it readily self-associates which induces the solution to phase separate.

This paper presents experimental investigation of the effect of two cosolvents, methanol and acetone, on the cloud-point behavior of poly(ethylene-*co*-acrylic acid) in ethylene to 260 °C and 2,500 bar. The poly(ethylene-*co*-acrylic acid) copolymers investigated contain 2.4 mol% (EAA_{2.4}), 3.9 mol% (EAA_{3.9}), 6.9 mol% (EAA_{6.9}), and 9.2 mol% (EAA_{9.2}) acrylic acid in the backbone.

EXPERIMENTAL

Cloud points measured at a fixed copolymer concentration of ~15 wt%, which is the expected maximum in the pressure-composition curve [Lee et al., 1994b; Irani and Cozewith, 1986], are obtained by using a high-pressure, variable-volume view cell described in detail elsewhere [Lee et al., 1994b; Meilchen et al., 1991]. Typically 0.350±0.002 g of copolymer are loaded into the cell which is subsequently purged several times at room temperature with ethylene to remove any entrapped air. Methanol and Acetone are transferred into the cell to within ±0.002 g with a syringe. Then, five-to-seven ±0.020 g of ethylene are transferred into the cell gravimetrically by using a high-pressure bomb. The system temperature is typically maintained to within ±0.2 °C below 200 °C, and to within ±0.4 °C above 200 °C.

Fig. 1 shows the typical change of opaqueness in the system caused by decreasing the pressure in the vicinity of the cloud point at fixed copolymer concentration. The copolymer solution in the cell is compressed to a single phase at a fixed temperature. The solution is maintained in the one-phase region at the desired temperature for at least 20 minutes so that the cell can reach thermal equilibrium. The pres-

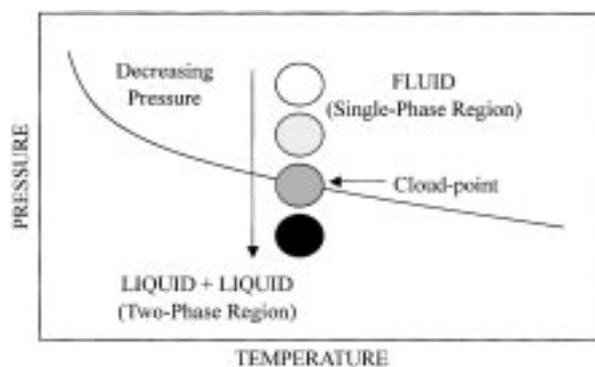


Fig. 1. Typical change of opaqueness in polymer solution caused by decreasing the pressure in the vicinity of the cloud point at fixed copolymer concentration.

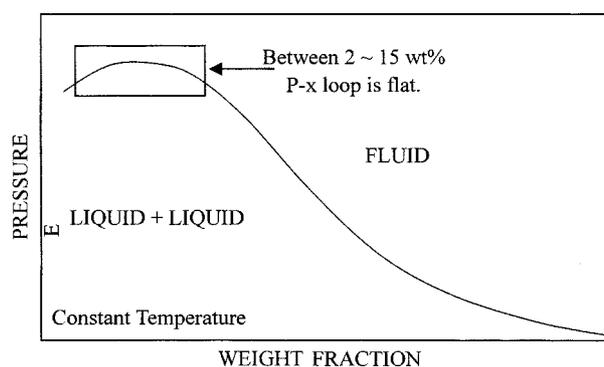


Fig. 2. Schematic pressure-polymer concentration (P-x) diagram at fixed temperature.

sure is then slowly decreased until the solution becomes cloudy. The cloud-point pressure is defined as the point at which the solution becomes so opaque that it is no longer possible to see the stir bar in the solution. The cell is then repressurized to a single phase, at least 150 bar above the cloud-point pressure, and maintained for at least 10 minutes. The cloud points are repeated at least twice at each temperature, and are typically reproducible to within ±5 bar at the highest temperatures. In the region where the cloud-point pressure increases very rapidly for a small change in temperature, the cloud points are reproducible to within ±10 bar. The lowest temperature of the cloud-point curves presented in this work represents either the highest operating pressure of the experimental apparatus or the location of the copolymer crystallization boundary. Fig. 2 shows the pressure-polymer concentration diagram at fixed temperature. Cloud-point pressures of the copolymer solutions have maxima between 2 and 15 wt% polymer, suggesting that at these polymer concentrations, the cloud-point pressures are reasonably close to the true mixture-critical point [Lee et al., 1994b; Irani and Cozewith, 1986; Rätzsch et al., 1983, 1982]. Therefore, cloud-point pressures are measured at fixed copolymer concentrations ~15 wt% in this study.

MATERIALS

The polyethylene, poly(ethylene-*co*-2.4 mol% acrylic acid), poly(ethylene-*co*-3.9 mol% acrylic acid), poly(ethylene-*co*-6.9 mol%

acrylic acid), and poly(ethylene-*co*-9.2 mol% acrylic acid) were obtained from E. I. DuPont de Nemours, Inc. Ethylene, methanol, and acetone with a minimum purity of 99.5%, were obtained from Aldrich Chemical Company and were used as received.

RESULTS

The location of the cloud-point curve in P-T space depends on the intermolecular forces between solvent-solvent, solvent-polymer segment, and polymer segment-segment pairs in mixture, and on the free volume difference between the polymer and the solvent. When cosolvent is added to polymer mixtures, interactions (i.e. intermolecular forces) between cosolvents and other solvent or polymer segment should be also considered.

Ethylene is chosen since it is the primary solvent and reactant used in the high pressure, free radical copolymerization of EAA. Ethylene is non-polar solvent so polar interactions with acrylic units in EAA are not expected. However, ethylene can be a proton acceptor due to π -electrons of double bond. Methanol is a strong polar solvent which has a large dipole moment of 1.7 Debye [Reid et al., 1987]. Methanol hydrogen bonds with both other methanol molecules and acrylic acid segments in EAA, while acetone, which is a basic molecule, does not hydrogen bond to itself. Using these two cosolvents, it is possible to ascertain the saturation effect of hydrogen bond. Table 1 lists the properties of PE, and four EAA copolymers. Although the molecular weight polydispersities are fairly large for these copolymers, previous studies show that the acid content has a much larger effect on the cloud-point behavior than does molecular weight polydispersity [Lee et al., 1994a]. Table 2 lists the properties of ethylene and the two cosolvents used in this study, acetone and methanol [Prausnitz et al., 1986; Reid et al., 1987].

Fig. 3 presents the cloud-point behaviors of PE, EAA_{2.4}, and EAA_{3.9}. The single phase region of EAA copolymers reduces as the acrylic acid content of EAA copolymers increases, due to self-association of acrylic acid segments. The self-association of acrylic acid segments is unfavorable to mixing EAA in ethylene. The energy of hydrogen bonding between acrylic acid segments is 11.5 kcal/mol [Otoka and Kwei, 1968]. This self-association is so strong that incorporating only 2.4 mol% acrylic acid into polyethylene in-

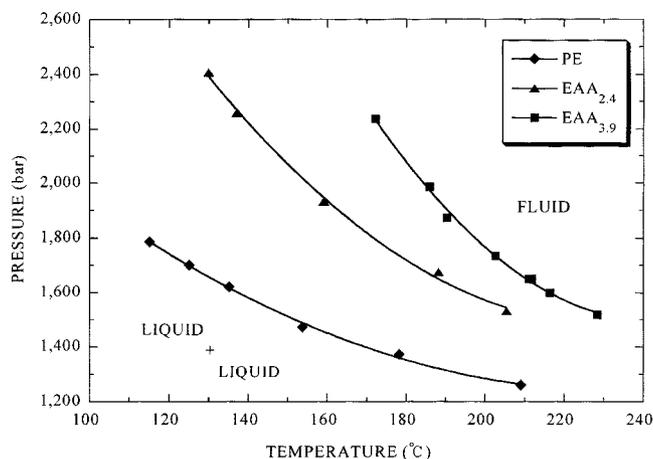


Fig. 3. Cloud-point curves of Polyethylene, EAA_{2.4}, and EAA_{3.9} in ethylene. EAA_{6.9} does not dissolve in ethylene even at 260 °C and 2,500 bar. The copolymer concentrations in solutions are ~15.0 wt%.

creases pressure to dissolve EAA_{2.4} by ~400 bar compared to the pressure to dissolve PE in ethylene at 170 °C. Fig. 3 shows that all the cloud-point pressures increase with decreasing temperatures. The negative slope of cloud-point curves is more severe as the acrylic acid content of EAA increases since the strength of hydrogen bonding is increased with decreasing temperatures, and the amount of self-association increases with the acrylic acid content of EAA. EAA_{6.9} did not dissolve in ethylene even at 260 °C and 2,500 bar.

Fig. 4 demonstrates the cosolvent effect of 7.6 wt% acetone on the cloud-point behavior of EAA - ethylene mixtures. Acetone has a large dipole moment of 2.9 Debye. Due to the large dipole moment of acetone, polar interaction is expected between acrylic acid and acetone. But the contribution of the polar interaction to dissolving EAA in the mixed solvent of ethylene and acetone is negligible, since there is less than 6.9 mol% acrylic acid segment in the EAA which is present at a concentration of ~15 wt% in solution. Acetone is a strong proton acceptor, not donor. A single carbonyl group of acetone molecule is assumed to interact with a single hydroxyl site on one acrylic acid segment.

Table 1. Physical properties of polyethylene (PE), poly(ethylene-*co*-2.4 mol% acrylic acid), poly(ethylene-*co*-3.9 mol% acrylic acid), poly(ethylene-*co*-6.9 mol% acrylic acid), and poly(ethylene-*co*-9.2 mol% acrylic acid) used in this study. The molecular weights of poly(ethylene-*co*-acrylic acid) are based on PE standards and are corrected for the acid content of the copolymer

Polymer	Acid content (mol%)	Crystallinity (%)	T _m	M _n	M _w	M _w /M _n
PE	0.0	42.0	123.0	21,000	106,000	5.1
EAA _{2.4}	2.4	37.5	108.0	19,100	100,050	5.2
EAA _{3.9}	3.9	36.3	100.7	21,000	123,100	5.9
EAA _{6.9}	6.9	26.3	90.5	13,400	59,700	4.5
EAA _{9.2}	9.2	19.5	83.6	11,100	33,800	3.0

Table 2. Physical properties of the solvent and cosolvents used in this study [Prausnitz et al., 1986; Reid et al., 1987]

Components	T _c (°C)	P _c (bar)	ρ _c (g/cm ³)	μ (debye)	Proton acceptor/donor
Ethylene	9.2	50.4	0.217	0.0	Weak acceptor
Acetone	234.9	47.0	0.278	2.9	Strong acceptor
Methanol	239.5	80.9	0.272	1.7	Strong acceptor & donor

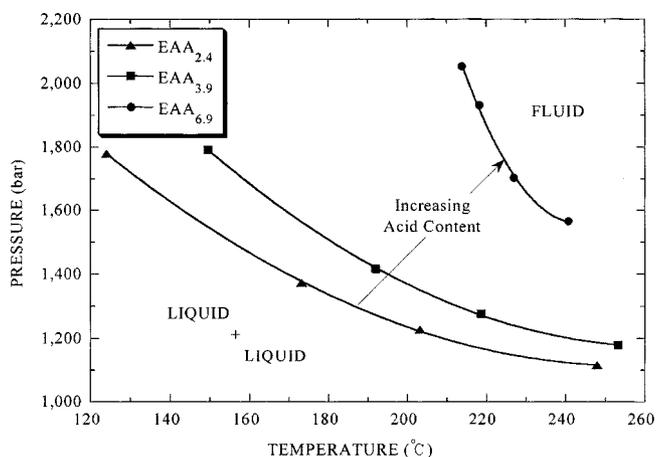


Fig. 4. Cosolvent effect of 7.6 (± 0.1) wt% acetone on the cloud-point curves of EAA_{2,4}, EAA_{3,9}, and EAA_{6,9} in ethylene. The copolymer concentrations in solutions are 14.1-15.0 wt%.

Cloud-point behavior of EAA with acetone is similar to the behavior of the copolymer in pure ethylene. The cloud-point pressures of EAA copolymers increase with decreasing temperatures in mixed solvent of acetone and ethylene. However, the single-phase region of EAA in the mixed solvent is greatly enlarged compared to the region in pure ethylene. For instance, at 180 °C adding only 7.6 wt% acetone into EAA_{3,9} - ethylene mixture decreases the cloud-point pressure of the copolymer solution by ~580 bar. EAA_{6,9}, which was not dissolved in pure ethylene, is now dissolved at temperatures below 240 °C and pressures under 2,100 bar. The increasing miscibility of EAA in the mixed solvent results from cross-associations between acrylic acid segments and acetone molecules. The cloud-point curves of EAA in the mixed solvent shift to high pressures and temperatures with acrylic acid content of EAA, suggesting that the cloud-point behavior of EAA has more influence on the self-associations of acrylic acid segments than cross-associations between acrylic acid segments and acetone molecules.

Fig. 5 shows the cosolvent effect of 5.9 wt% methanol on the cloud-point behavior of EAA - ethylene mixtures. Methanol has a

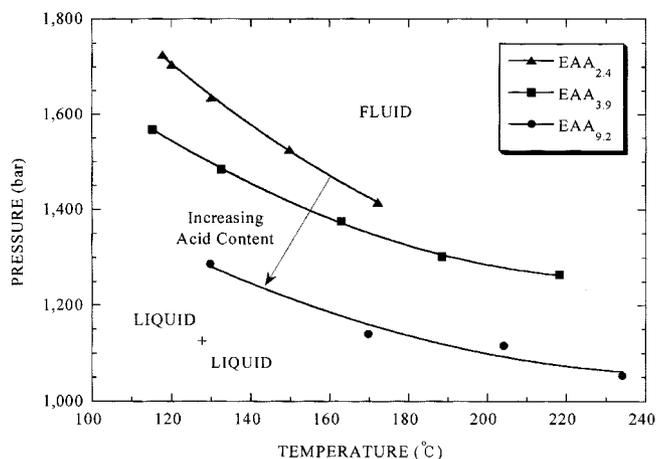


Fig. 5. Cosolvent effect of 5.9 (± 0.4) wt% methanol on the cloud-point curves of EAA_{2,4}, EAA_{3,9}, and EAA_{9,2} in ethylene. The copolymer concentrations in solutions are 14.5-15.1 wt%.

large dipole moment of 1.7 Debye, but more importantly for this study, methanol acts as both a proton donor and acceptor. The similar temperature-dependent behavior shown in EAA - ethylene and EAA - ethylene - acetone mixtures is observed in EAA - ethylene - methanol mixtures. However, the single-phase region of EAA copolymers enlarges with the acrylic acid content in the mixed solvent of methanol and ethylene, while the single-phase region of the copolymers shrinks with increasing the acrylic acid content in mixed solvent of acetone and ethylene. The cosolvent effect of methanol on the miscibility of EAA is more noticeable than the effect of acetone. Adding 5.9 wt% methanol to EAA_{3,9} - ethylene mixture decreases the cloud-point pressure by 770 bar at 180 °C. This better cosolvent effect of methanol can be attributed to molecular structures of acrylic acid segment and methanol. One acrylic acid segment can make two hydrogen bonds with a methanol molecule, since both the carbonyl group and hydroxyl group in acrylic acid segment can participate in cross-association with the hydroxyl hydrogen and the oxygen in methanol molecule. It is supposed one acrylic acid segment cross-associates with two or three methanol molecules. The number of cross-associations between acrylic acid and methanol can be 2-3 times more than the number of acrylic acid segments of EAA, suggesting that pressures to dissolve EAA in ethylene - methanol mixed solvent decrease with increasing acrylic acid content in EAA.

Fig. 6 shows the diminishing effect of methanol cosolvent on the cloud-point behavior of EAA_{2,4} - ethylene solution. Since methanol acts as both a proton donor and acceptor, the phase behavior of EAA_{2,4} - ethylene - methanol mixture is influenced by three different types of hydrogen bonding: the cross-association of methanol molecules and the acrylic acid segment of EAA, the self-association of the acrylic acid segments, and the self-association of methanol molecules. While acrylic acid self-association and methanol self-association are unfavorable for dissolving EAA, the cross-association of acrylic acid segments and methanol is favorable to mixing. As the methanol concentration in the mixed solvent increases, the probability of methanol self-association becomes greater than the probability of cross-association since there are only 2.4 mol% acid segments in the copolymer which is present at a concentration

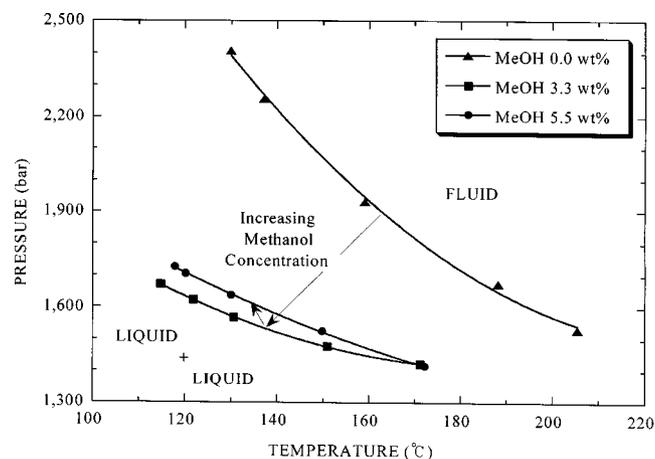


Fig. 6. Cosolvent effect of methanol on the cloud-point curves of EAA_{2,4} in ethylene. The copolymer concentrations in solutions are ~15.0 wt%.

of ~15 wt% in solution. A subtle balance exists between the cross-association of methanol with EAA_{2,4}, the self-association of the acrylic acid segments, and the self-association of methanol. Therefore interpreting the phase behavior of the EAA_{2,4} - ethylene - methanol mixture is expected to be more complicated compared to the behavior of the EAA_{2,4} - ethylene - acetone solution.

Adding 3.3 wt% methanol to EAA_{2,4} ethylene solution reduces the pressure dissolving EAA_{2,4} from 2,200 to 1,520 bar at 140 °C. At the concentration of 3.3 wt% methanol, the ratio of moles of methanol to moles of acrylic acid is 8.3. Since one acrylic acid segment is supposed to interact with 2-3 methanol molecules, the bulk of the acrylic acid segments are expected to be cross-associated with methanol molecules. The self-association of methanol molecules begins to unfavorably affect the phase behavior of EAA_{2,4}-ethylene-methanol solution. Interestingly, the addition of 5.5 wt% methanol raises the cloud-point pressure to 1,580 bar at 140 °C, which is an indication that methanol acts as antisolvent. At 5.5 wt% methanol, the ratio of moles of methanol to moles of acrylic acid is 14.5. All of the acrylic acid segments are expected to be "saturated" by methanol molecules and the self-association of methanol influences more unfavorably the phase behavior of the copolymer solution. The nature of methanol changes from cosolvent to antisolvent as the concentration of methanol is greater than ~5.5 wt%.

Fig. 7 shows the cloud-point behavior of EAA_{3,9}-ethylene-methanol mixture and demonstrates the diminishing effect of methanol more obviously. In P-T space, single-phase region of EAA_{3,9}-ethylene-methanol solution increases with the methanol concentration to 9.1 wt% methanol. The extent of enlarging single-phase reduces with increasing methanol concentration. For instance, at 180 °C the addition of 2.9 wt% methanol decreases the cloud-point pressure by 490 bar. Adding 3.6 wt% more methanol to 6.5 wt% decreases the cloud-point pressure by 260 bar. Adding 9.1 wt% methanol only reduces the cloud-point pressure by 50 bar. However, 6.5 wt% methanol acts as cosolvent to EAA_{3,9}-ethylene mixture, whereas 5.5 wt% methanol does as antisolvent to EAA_{2,4}-ethylene mixture. The number of acrylic acid segments of EAA_{3,9} is 1.6 times the number of acrylic acid segments of EAA_{2,4}, suggesting that EAA_{3,9} can seize 3.2-4.8 times more methanol molecules than does EAA_{2,4} before

methanol reverses to antisolvent. At the concentration of 9.1 wt% methanol the ratio of moles of methanol to moles of acrylic acid is 14.6, which assumes that all of the acrylic acid segments already associate with methanol molecules and methanol molecules are available to self-association. The phase behavior of EAA_{3,9}-ethylene-methanol mixture is now dominated by the self-association of methanol. It should be noted that all of the cloud-point curves converge as temperature increases. Since hydrogen bonding is weakened at high temperatures [Lee and McHugh 1997; Lee et al., 1994b; Otoka and Kwei, 1968; Earnest and MacKnight, 1980], the cross-association between acrylic acid and methanol, the self-association of acrylic acid, and the self-association of methanol become negligible. Therefore EAA copolymers behave as non-polar polyethylene and the mixed solvent of methanol and ethylene does as non-polar ethylene.

CONCLUSIONS

Even though the EAA copolymers used in this study had only 2.4-9.1 mol% acrylic acid segments in the backbone structure, the region of miscibility in the mixed solvent of ethylene-cosolvent decreases significantly with decreasing temperature due to strong self-association of the acrylic acid of EAA at low temperatures. Both cosolvents investigated, acetone and methanol, that cross associate with the acrylic acid segments, dramatically enlarge the single-phase region of this copolymer compared to the region in pure ethylene. At low concentrations, methanol is a better cosolvent than acetone, since methanol cross-associates with both carbonyl oxygen and hydroxyl hydrogen of acrylic acid segments. However, the impact of methanol cosolvents diminishes rapidly with increasing cosolvent concentrations since there are only a finite number of acrylic acid segments that can participate in hydrogen bonding. At high concentrations, methanol reverses to antisolvent due to unfavorable interactions between excess methanol molecules, which increase once all the acrylic acid segments in EAA are saturated with methanol.

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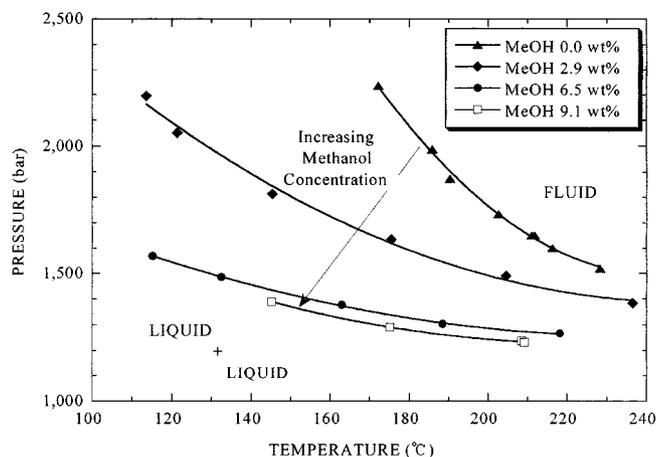


Fig. 7. Cosolvent effect of methanol on the cloud-point curves of EAA_{3,9} in ethylene. The copolymer concentrations in solutions are ~15.0 wt%.

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